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Recovery sub micron-graphitized carbon from oil fly ash

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Oil fly ash is known as one source of raw materials from which vanadium and nickel metals can be recovered. The current recovery process of valuable metals from oil fly ash is mainly the hydrometallurgy one. Nevertheless, a great amount, about 50~80%, of unburned carbon remains as byproduct after hydrometallurgy process. In Taiwan, if hydrometallurgy processes have proceeded, it can be estimated that the annual production of unburned carbon is 25 thousand tons. From the viewpoint of resource recycling, this study is a preliminary study and investigates in recovery of sub micron- graphitized carbon from unburned carbon by a designed process. The designed process included the following steps: 1.selecting a portion with +400mesh size from unburned carbon; 2.treating the selected in ultrasonic waves; 3.using a 400mesh sieve to obtain the product which is under 400mesh; 4.Removal ash from the product. In regard to treatment by ultrasonic waves in the designed process, treating time of ultrasonic waves is a simple and only variance in this study. The results indicate that the production yields increase with the treating time of ultrasonic waves; the production yield in specific conditions of this study can reach about 23%, in which ash content in product is about 2.5%. According to results of SEM, TEM and XRD, the products from the designed process are flakes in shape, several microns in size and graphitized carbon in carbon crystal phase. Except to graphitized carbon, there are a little carbon blacks, which are graphite 2H in carbon crystal phase in the products. Conclusively, the designed process is possibly applicable, by which comes to the recovery of micron- graphitized carbon.

Key words: oil fly ash; unburned carbon; graphitized carbon

Introduction

Oil fly ash is known as one source of raw materials from which vanadium and nickel metals can be recovered. The current recovery processes of valuable metals from oil fly ash are mainly the hydrometallurgy ones. Nevertheless, a great amount, about 50~80%, of unburned carbon remains as byproduct after hydrometallurgy processes. According to reference data [1], the annual production of oil fly ash is 43 thousand tons (about 2.9kg in burning per kiloliter of heavy oil). In Taiwan, if hydrometallurgy processes have proceeded, it can be estimated that the annual production of unburned carbon is 25 thousand tons [2].

Because unburned carbon is a puffy powder with tiny carbon particles, it is like a carbon resource. It is also, however, a possible environmental pollutant. To prevent pollution, unburned carbon are presently either disposed in landfills or burned as fuel. But, both landfills and burning hold no economic benefits. Landfills waste ground space and spend disposal costs on burying a carbon resource. The burning process encountered problems of low-combustion efficiency because unburned carbon has a high ignition point does not burn well in common furnaces [3]. Therefore, it is necessary to search for new ways to use unburned carbon or find more economical treatments of unburned carbon taking into consideration its innate characteristics.

According to characteristics of unburned carbon [4], it is made up of carbon particles whose size range from a certain μm to 300 μm, as shown in Fig. 1(A). Carbon particles can be divided into two types, based on their external appearance [5]: the porous and the foamed types as Fig. 1(C) and (D). Furthermore, carbon crystal phases in these particles are regarded as amorphous carbon, graphitized carbon and graphite 2H, JCPDs number41-1487. The relationships between these two types of carbon particles and crystal phases are as following: amorphous carbon and graphitized carbon are the major crystal phases that consist of two types of carbon particles. Nevertheless, there is a higher percentage of amorphous carbon in the porous type than in the foamed one. In addition, some spherical particles found by TEM are carbon blacks and their carbon crystal phases are regarded as graphite 2H by undertaking the electron diffraction analysis. Besides, the mechanical resistance of the porous and the foamed particles is different when crumbled with ultrasonic waves. As shown in Fig. 1(B), when being crumbled by ultrasonic waves, the foamed particles are almost destroyed while the porous particles remain the same.

Because the lubricity of graphite, fine graphite are hard to manufactured by traditional mills. It results high manufacture costs and prices [6]. A vast amount of raw material, sub micron- graphitized carbon, may be significantly helpful for the manufacture processes of fine graphite. Therefore, based on the mentioned difference of mechanical resistance and crystal phases between the foamed and the porous type of carbon particles, the purpose of this study is to recover graphitized carbon from the foamed type by a designed process such as the shown in Fig. 2. In the designed process, the treatment by ultrasonic waves is the keyword that mainly affects the

foamed type of carbon particles and functions to reduce sizes. So, experiments in this study focus on the treatment by ultrasonic waves, and results including chemical composition, production yields, carbon crystal phases and sizes of products are analyzed. Through this preliminary study, some developments of resource recycling may continue applying on unburned carbon from oil fly ash.

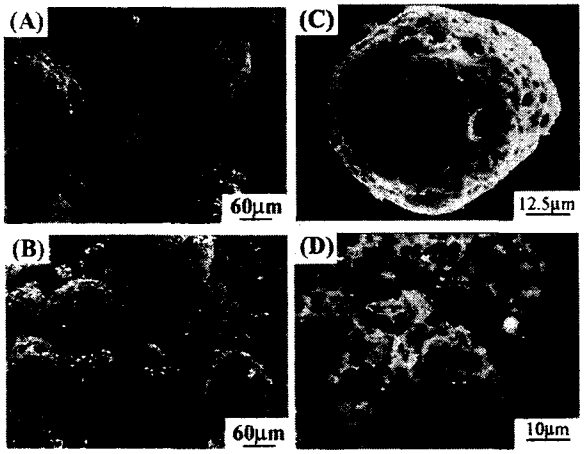

Fig. 1SEM Images of unburned carbon.

(A)unburned carbon; (B)unburned carbon after being treated by ultrasonic waves; (C)the porous particle in unburned carbon; (D)the foamed particle in unburned carbon.

Experiment

The experimental flowchart in this study was showed in Fig. 2. The followings were descriptions:

Source of oil fly ash

Oil fly ash was sampled from an oil-burning boiler that functioned to generate electric power in Northern Taiwan and was equipped with electrostatic precipitators to capture fly ashes.

Preparation of unburned carbon by leaching

In order to obtain unburned carbon, oil fly ash was pretreated as the following steps and conditions: first, leaching oil fly ash in 2N sulfuric acid at a ratio of 10g/50ml and stirring at a speed of 200rpm for 2 hours at 30℃; after leaching, the filter cake as well as unburned carbon was separated from the leaching solution by pumping filtration; next, refining unburned carbon with water; and finally, drying it at 105℃ for 24 hr. Besides, the leaching solution was sent to hydrometallurgy processes for recovery valuable vanadium and nickel compounds.

The Designed process and experimental conditions

Before the treatment by ultrasonic waves, -400 mesh portion of unburned carbon was pre-removal by wet sieving in 95% alcohol solution because of its high ash content, about 14.3%. And, +400 mesh portion was the selected portion and adjusted concentration as 20g solid/200ml alcohol solution for the next treatment of ultrasonic waves. The ultrasonic launching device, Sonics & Materials VCX600 (frequency: 20Hz, about 30% of output power: 30W, diameter of probe head: 13mm, swing of probe tip: 107 μ m) was operated to pulverize the foamed type of carbon particles but the porous one. This study varied the treating time of ultrasonic waves, 0.5, 1, 4, 7, and 10mins. After treatments by ultrasonic waves, a sieve with 400mesh was used again to remove the porous particles that were larger than 37 μ m. And, the –400mesh portion was collected and dried. Then, aqua regia was used to remove undesired ash. With numerous times of refining in water and final drying, the crumbled flakes were products from the foamed particles. Then, production yields were calculated in according of weight measurements. Finally, the products were observed and analyzed by SEM, XRD, Laser particle size distributor, and Elemental analyzer.

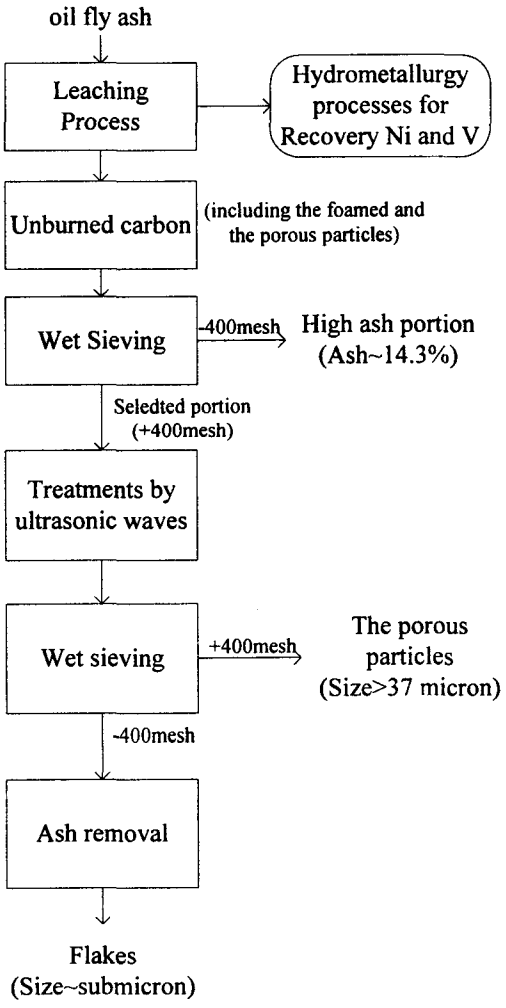

Fig. 2 Experimental flowchart

Analytic apparatus

A Heraeus Rapid Elemental Analyzer was used to analyze C, H, N and S contents in the samples. Ash contents were calculated as the residual percentages in which samples were burned in air at 800℃ for 24hr. XRD patterns were obtained with a Siemens D5000 diffractometer using Cu kα 1(λ =1.5406Å) radiation. The thin powder samples were placed on an oriented mono-crystalline quartz plate and scanned from 10 to 90°2θ at a speed of 2°/min and signals were recorded at intervals of 0.02 ° 2 θ . Peak positions was determined through determined of the X-ray peaks with a combination of Gaussian profiles as determined by using the Siemens Diffrac AT software provided with the diffractometer. A Hitachi S-4200 electron microscope was used for the SEM imaging investigation. Because of the electronic conductivity of unburned carbon samples, observation samples were directly fixed on the adhesive tapes that can conduct electricity to samples. The TEM (Hitachi FE-2000) was used for selected areas electronic diffraction (SAED), so that the crystal phases could be analyzed. Disaggregating the observation sample in ethanol, imbibing the up layer of the disaggregation, allowing it to drip onto a copper sieve with a 3mm diameter, and at last drying the wafer at room temperature. A laser particle size distributor, Shimadzu, Sald-2001, was employed to analyze samples that are suspended in 95% ethanol.

Results and Discussion

Appearance of products

After unburned carbon was proceded by the designed process, SEM was used to observe the products directly. In the SEM images, all products treated by different time of ultrasonic waves showed similar external appearance that were mainly crumbled flakes from the foamed particles and a little carbon black particles, as shown in Fig. 3, which corresponded to Fig. 1(B). The crumbled flakes were several microns in size, and the particle diameters of carbon blacks were far finer than the flakes. Both of them showed some aggregations in SEM images.

Particle size

A laser particle size distributor was used to measure the products. The mean particle size of products with different treating time of ultrasonic waves were among 5~8 microns and showed no tendency with the treating time. This result was easily caused by aggregations of small particles that were mentioned in above. In addition, a noticeable common point was that the different curve in graphs displayed two peaks, as in Fig. 4: one was 2~5 microns in size and another was 5~20 microns in size. However, these results did not correspond with the particle sizes in SEM observations. It was recognized that there were some analytic difficulties in dispersing fine particles at sample preparations. Although, the problem of aggregation was not yet overcome in this study, it was justness that the actual particle size would be smaller than the present results. Over and above, the dispersion of products would be the key points in future research for both measurements and future utilizing.

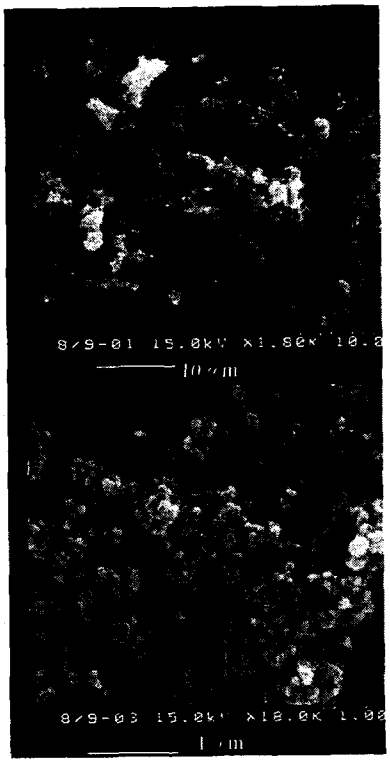

Fig. 3 SEM images of crumbled flakes (the above) and carbon blacks (the below) in products treated at 0.5mins.

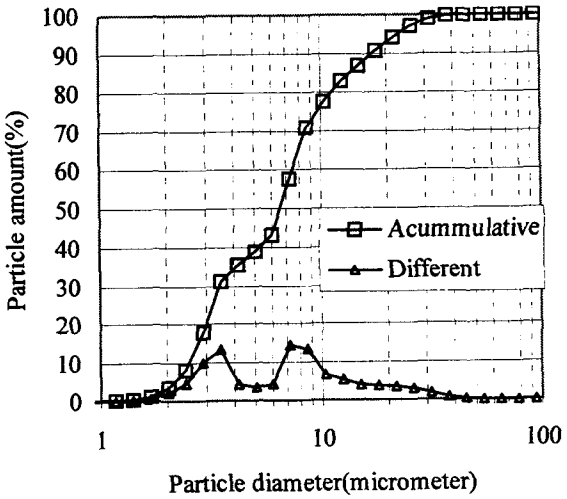

Fig. 4 Particle size distribution of the products.(Treating time of ultrasonic waves = 0.5mins)

Carbon crystal phases

According to previous research of authors [5], the carbon crystal phases of unburned carbon were graphitized carbon, graphite 2H and amorphous carbon by profile

fitting analyses. The amorphous carbon kept more percent in the porous type of carbon particles. In the designed process of this study, the products should be the crumbled flakes mostly from the foamed type of carbon particles. In order to confirm the crystal phases, both products and the porous particles from the designed process were analyzed by XRD. In order to illustrate both of their carbon crystal phases, the XRD patterns were shown in Fig. 5. Approximately, the results agreed with the above that the products with different treating time of ultrasonic waves existed carbon crystal of graphitized carbon and graphite 2H. And, the porous type of carbon particles was crystal phases of graphitized carbon, graphite 2H and amorphous carbon.

Because there were two carbon crystal phases existing in products, the distribution of each phase was concerned. As in Fig. 5(B), the graphite 2H was d-spacing about 3.9 angstrom. It was the crystal phase of carbon blacks according to JCPDS cards. The images and patterns in TEM were evidenced as Fig. 6(B). Carbon blacks were spheres in shape and their patterns were diffuse ring of (002) and (100) planes. The graphitized carbon was d-spacing about 3.4 angstrom. The TEM images and Diffraction patterns were as Fig. 6(A). The patterns of (002), (100), (004) and (110) plane in graphitized carbon were distinct lenticular. The graphitized carbon could potentially approach the ideal crystal structure of graphite after graphitization at high temperature according to the definitions of Franklin [7]. Based on SEM results, such as Fig. 3, carbon blacks and crumbled flakes could be distinguished easily. It indicated that two of the phases, graphitized carbon and graphite 2H, were not entirely locked to each other, and were possible to separate. So, remove of carbon blacks might be the further step in order to use as special graphite materials.

Production yields and chemical compositions of products

In all the experimental results of the designed process, only the production yields and compositions of products changed as the treating time of ultrasonic waves obviously. In Table. 1, the production yields increased as the treating time of ultrasonic waves. The yield after removal ash reached a maximum, about 23%, at 7 mins at fixed ultrasonic conditions of this study. Carbon contents were main component in products, which were more than 90%, and increased as treating time slightly. Other elements such as nitrogen, sulfur and hydrogen were minor components, in which nitrogen was about 1.5%, sulfur was about 1.0% and hydrogen was about 0.3%. Because of the less of the above elements, it showed that the products could not react with concentrated acid even in the erosion of aqua regia.

The ash contents on products were not too different, about 3.2~2.5%, after ash removal by aqua regia. This result implied that ashes in products were not exposed and the amounts of inner ashes were about 2.5% in the flakes.

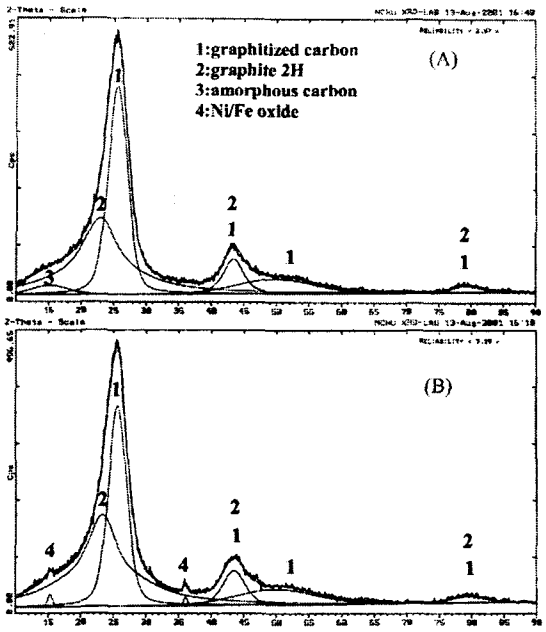

Fig. 5 The XRD plots of (A) the porous type; (B) the products after being deleted ashes.

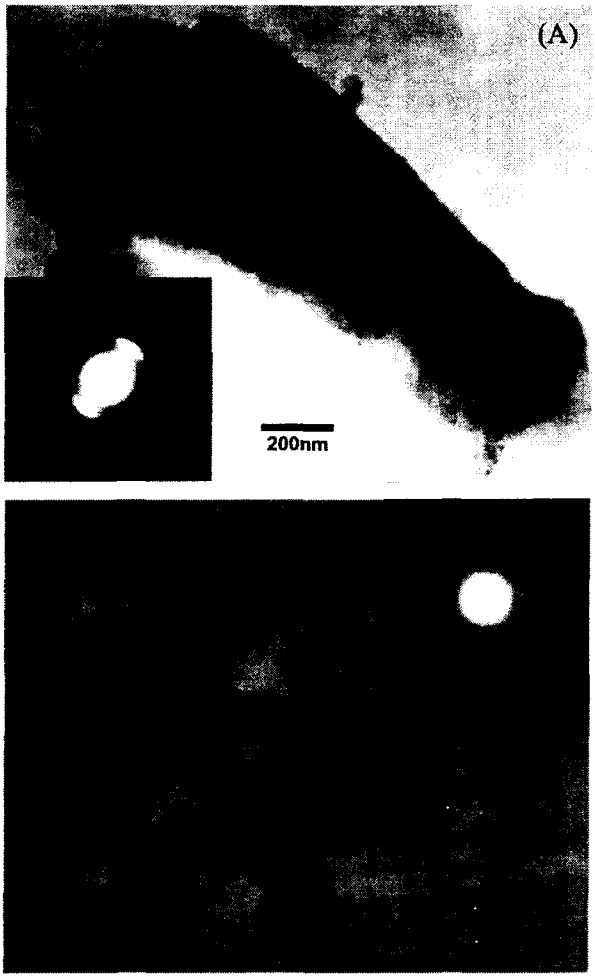

Fig. 6 TEM images and diffraction patterns of (A) crumbled flakes and (B)carbon blacks.

Table. 1 The recovery yield and chemical compositions of products after removal ash.

Treating time of ultrasonic waves (min)	Yield (%)	Compositions (%)				
		C	N	S	H	Ash
0.5	11.6	90.1	1.6	1.0	0.4	3.2
1	13.9	90.5	1.5	1.0	0.3	3.0
4	20.7	92.1	1.7	1.0	0.4	2.9
7	23.3	92.6	1.6	1.0	0.3	2.5
10	23.0	92.7	1.6	1.0	0.4	2.5

Conclusion

The designed process to recovery micron graphitized carbon is practicable. The production yield in specific conditions of this study can reach about 23%, in which ash content in product is about 2.5%. According to results of SEM, TEM and XRD, the products from the designed process are flakes in shape, several microns in size and graphitized carbon in carbon crystal phase. Except to graphitized carbon, there are a little carbon blacks, which are graphite 2H in carbon crystal phase in the products. With the rudimentary results, following researches will concentrate on the control the crumbling of ultrasonic waves, the mechanism of the crumbling of the foamed type and also the dispersion of products with sub micron in size.

Acknowledgment

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